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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT INITIATION

Date: September 1, 1972

Project Title: "Simple and Complex Metal Hydrides"

Project No: G-33-655

Principal Investigator: Dr. E. C. Ashby

Sponsor: American Chemical Society, Petroleum Research Fund

Agreement Period: From September 1, 1972 Until August 31, 1975

Type Agreement: Grant No. PRF # 3211-AC4

Amount: $20,000

Reports Required: Annual Progress Reports
Final Summary Report

Sponsor Contact Person (s):
Mr. Justin W. Collat
Program Administrator
The Petroleum Research Fund
American Chemical Society
1155 Sixteenth Street, N.W.
Washington, D. C. 20036

Assigned to: Chemistry

COPIES TO:

- Principal Investigator
- School Director
- Dean of the College
- Director, Research Administration
- Director, Financial Affairs (2)
- Security-Reports-Property Office
- Patent Coordinator
- Library
- Rich Electronic Computer Center
- Photographic Laboratory
- Project File
- Other

RA-3 (6-71)

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

No action

Date: December 15, 1976

Project Title: Simple and Complex Metal Hydrides

Project No: G-33-655

Project Director: Dr. E. C. Ashby

Sponsor: American Chemical Society; The Petroleum Research Fund

Effective Termination Date: 8/31/76

Clearance of Accounting Charges: 8/31/76

Grant/Contract Closeout Actions Remaining: none

_ Final Invoice and Closing Documents
_ Final Fiscal Report
_ Final Report of Inventions
_ Govt. Property Inventory & Related Certificate
_ Classified Material Certificate
_ Other _____

Assigned to: Chemistry (School/Laboratory)

COPIES TO:

Project Director
Division Chief (EES)
School/Laboratory Director
Dean/Director—EES
Accounting Office
Procurement Office
Security Coordinator (OCA) ✓
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Library, Technical Reports Section
Office of Computing Services
Director, Physical Plant
EES Information Office
Project File (OCA)
Project Code (GTRI)
Other _____

CA—4 (3/76)

G-33655
AP #1

Stereochemistry of Hydride Reductions

Our efforts during the past year have been along three lines of research involving reductions of cyclohexanones (1) reduction with i-Bu_2AlH and i-Bu_3Al (2) reductions with $LiAl(i\text{-}Bu)_3n\text{-}Bu$ and (3) reductions with a wide variety of known complex metal hydrides. Summaries of the results from the three projects follow:

(1) The reduction of 3,3,5-trimethylcyclohexanone and 4-tert-butylcyclohexanone with diisobutylaluminum hydride (DIBAH) and with triisobutylaluminum (TIBA) has been examined in ether and in benzene. Reduction of these ketones with DIBAH in 1:1 stoichiometry produces the epimeric alcohols in quantitative yield. The isomer ratio of the product mixture is essentially independent of solvent and reactant stoichiometry. On the other hand, reduction of these ketones with TIBA is more selective and is accompanied by some (ca. 5%) enolization. The isomer ratio of the product mixture is essentially independent of solvent, but dependent on the reactant stoichiometry and the initial concentration of TIBA. Evidence is presented which indicates that the epimeric ratio of alcohol products is influenced by the degree of association of TIBA, complex formation between TIBA and the aluminum alkoxide formed, and isomer equilibration by a Meerwein-Ponndorf-Verley pathway.

(2) Lithium triisobutyl-n-butylaluminate (LTA) was prepared by reaction of n-butyllithium with triisobutylaluminum. Reduction of 3,3,5-trimethylcyclohexanone with LTA in benzene gave a mixture of epimeric alcohols containing 97% of the trans isomer, while reduction of 4-t-butylcyclohexanone with LTA in ether or benzene led to a mixture of

alcohols containing 47% of the trans isomer. In all cases reduction was accompanied by 0-3% alkylation, but formation of aluminum enolate was not observed. Unlike the results obtained from reduction of those ketones with triisobutylaluminum, the stereochemical composition of the product mixture from LTA reduction was independent of reactant stoichiometry, concentration of reducing agent, and the nature of the solvent.

(3) The stereochemistry of reduction of several ketones by a variety of metal hydrides was investigated. The results are discussed in terms of steric approach control, torsional strain, compression effect, and change in conformation of the ketone. The stereochemistry of reduction of $MAlH_4$ is shown to be dependent on M^+ and concentration. Comparison of $LiAlH_4$ and $LiBH_4$ show $LiBH_4$ to be less subject to steric hinderance. Reduction of 2-methylcyclohexanone with $ClMgAlH_4$ and $Mg(AlH_4)_2$ give results best explained by complexing the carbonyl oxygen with Mg^{++} and by a change in the conformation of the ketone. Results from reductions of cyclopentanones and cis-2-methyl-4-tert-butylcyclohexanone do not suggest the presence of a compression effect for metal hydride reduction. A study of $LiAl(OR)_3H$ stereochemistry showed it to be independent of concentration. Several new and other hydrides are investigated as reducing agents. Stereochemical results with $LiAlD_4$ and $LiAlH_4$ are found to be the same.

G-33-655

August 4, 1975

Annual Progress Report

Dr. Justin W. Collat
Program Administrator
American Chemical Society
1155 SixteenthB Street, N.W.
Wahhington, D.C. 20036

Dear Dr. Collat:

Attached is a brief annual report concerning our work on mechanisms and stereochemistry of metal hydride reductions. I have requested our accounting office to supply you with the information requested in the Financial Statement and Personnel Statement.

Please let me know if I can be of any further assistance.

Sincerely yours,

E.C. Ashby
Regents' Professor of Chemistry

ECA:cb

BRIEF ANNUAL REPORT

PRF No. _____

TITLE OF GRANT _____

PRINCIPAL INVESTIGATOR E.C. Ashby

INSTITUTION Georgia Institute of Technology

Our efforts during the past year have been along two lines of endeavor: (1) a study of the mechanism of $LiAlH_4$ reduction of ketones and (2) development of a new reagent ($LiAlH_4$-CuI) to effect conjugate reduction of enones. Summaries of the two projects are as follows:

(1) Pseudo first order kinetic studies on the reaction of $LiAlH_4$, $NaAlH_4$ and $LiAlD_4$ with mesityl phenyl ketone have been carried out in tetrahydrofuran at 25°. The reactions were carried out in excess hydride and found to be first order in hydride and first order in ketone. $LiAlH_4$ is about ten times more reactive than $NaAlH_4$ which indicates the importance of the cation in the mechanism of the reaction. A deuterium kinetic isotope study involving the reaction of $LiAlH_4$ and $LiAlD_4$ with mesityl phenyl ketone gave a value of k_H/k_D of 1.27 which implicates the transfer of the hydride from aluminum to the carbonyl carbon in the rate determining step of the reaction. Entropies of activation for reduction of mesityl phenyl ketone by $LiAlH_4$ and $NaAlH_4$ indicate that the transition state is considerably more ordered for reduction by $LiAlH_4$ (-26.2 vs -5.4 eu) and that the transition state is of considerably lower energy (10.5 vs 18.1 kcal).

(2) Conjugate reduction of 2,2,6,6-tetramethyl-trans-4-hepten-3-one and mesityl and oxide by the new reagents $LiAlH_4$-CuI and $LiAlH_4$-$TiCl_3$ have been studied. The optimum conditions for conjugate reduction depend on the ratio of $LiAlH_4$:CuI (or $TiCl_3$):enone, temperature, solvent, and reaction time involving

$LiAlH_4$ and CuI or $TiCl_3$ before the enone is added. Enone I can be reduced in quantitative yield and 100% regioselectivity in 1 hr or less when the ratio of $LiAlH_4$:CuI:enone is 1:4:1, the solvent is THF and the temperature is 0°. Enone II can be reduced in 70% yield and 100% regioselectivity when the $LiAlH_4$:CuI:enone ratio is 1:4:0.5 in THF at 0° in 1 hour or less. Reduction of enones I and II with $LiAlH_4$-$TiCl_3$ proceeds with 100% regioselectivity, however the yields are lower (66 and 34% respectively) compared to the results obtained with the $LiAlH_4$-CuI reagent.

G-33-655

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

OFFICE OF
THE DIRECTOR OF
FINANCIAL AFFAIRS

January 19, 1977

American Chemical Society
1155 Sixteenth Street, N. W.
Washington, D. C. 20036

Gentlemen:

Enclosed is the original and one copy of the Final Financial Statement and Personnel Statement for PRF No. 3211-AC4.

If you have any questions or require additional information, please let us know.

Sincerely yours,

C. Evan Crosby
Associate Director of
Financial Affairs

CEC/bs
enclosures:

cc: Dr. E. C. Ashby with encl:
Dr. J. A. Bertrand with encl:
Mr. E. E. Renfro with encl:
Mr. A. H. Becker with encl:
File G-33-655

FINAL FINANCIAL STATEMENT
(Insert "Annual" or "Final", as appropriate)

AMERICAN CHEMICAL SOCIETY - THE PETROLEUM RESEARCH FUND

For the Period: September 1, 1972 to August 31, 1976.
(August 31 is the preferred closing date for the reporting period)

Balance at Start of Reporting Period		7,100.79
Received from PRF During Reporting Period		.00
Salaries to:		
Principal Investigator (Contribution toward summer salary*)	.00	
Graduate or Undergraduate Students	3,750.00	
Postdoctoral Fellows	.00	
_____	.00	
Fellowships or Scholarships to:		
Undergraduate Scholars	.00	
Graduate Fellows	.00	
Postdoctoral Fellows	.00	
Tuition	.00	
Materials and Supplies	2,305.50	
Equipment	.00	
Travel	398.25	
Other Expenses	647.04	
Institutional Supplement*	.00	
Departmental Supplement or Allocation*	.00	
* If provided in grant agreement		
Total Expenditures During Reporting Period	7,100.79	
Balance on Hand at End of Period		.00
Total of PRF Grant Payments Received to Date		19,400.00

Complete this section only for a FINAL FINANCIAL STATEMENT which shows a balance in the grant account.

The balance in the grant account will be liquidated

☐ By refund of unspent and uncommitted funds. The check should be drawn to the order of American Chemical Society - The Petroleum Research Fund, and identified by the number of the grant.

☐ By use in the completion of the grant project. We hereby request approval by the American Chemical Society of an extension of the grant agreement, without commitment of additional funds until _____, (period up to one year, renewable).

We certify that the expenses reported herein were incurred for education and research in accord with the terms of the approved ACS-PRF grant-in-aid.

Georgia Institute of Technology
(Grantee Institution)

By _____ C. Evan Crosby, Associate Director of Financial Affairs (Financial Officer) — January 19, 1977 (Date)

_____ _____ — 3211-AC4
(Name of Principal Investigator) (PRF No.)

** Please submit IN DUPLICATE to The Petroleum Research Fund - American Chemical Society, 1155 Sixteenth Street, N. W. Washington, D. C. 20036 **

PERSONNEL STATEMENT

PRF# 3211 - AC 4 REPORTING PERIOD September 1, 1972 TO August 31, 1976

GRANTEE INSTITUTION Georgia Institute of Technology DEPARTMENT Chemistry

PRINCIPAL INVESTIGATOR(S) E.C. Ashby

GRANT PROJECT TITLE Simple and Complex Metal Hydrides

List undergraduate, graduate, and postdoctoral co-workers receiving stipends under the above named grant:

NAME	TITLE OR ACADEMIC APPOINTMENT	PREVIOUS EDUCATION & DEGREES*	COUNTRY OF PERMANENT RESIDENCE	PERIOD OF SUPPORT (MONTHS)	PERCENT OF SUPPORT FROM PRF	DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD
Mr Ronnie Boone	Research Asst.	B.S. National Taiwan	Taiwan	8	100 %	Ph D
Mr. Jiang Lin	Research Asst.	B.S. David Lipscomb	USA	18	100 %	
Mr. Geo. Heinsohn	Research Asst.	Ph D	USA	12	100 %	

List other co-workers on grant project not directly supported with ACS - PRF funds:

NAME	SOURCE OF SUPPORT	DATES ASSOCIATED WITH GRANT PROJECT

* For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph. D. granting institution.